

# HETEROGENEOUS CHEMISTRY RELATED TO STRATOSPHERIC AIRCRAFT

## FINAL REPORT

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## INTRODUCTION

Emissions from stratospheric aircraft that may directly or indirectly affect ozone include  $\text{NO}_y$ ,  $\text{H}_2\text{O}$ , soot and sulfuric acid. To fully assess the impact of such emissions, it is necessary to have a full understanding of both the homogeneous and heterogeneous transformations that may occur in the stratosphere. Heterogeneous reactions on stratospheric particles play a key role in partitioning ozone-destroying species between their active and reservoir forms. In particular, heterogeneous reactions tend to activate odd chlorine while deactivating odd nitrogen. Accurate modeling of the net atmospheric effects of stratospheric aircraft requires a thorough understanding of the competing effects of this activation/deactivation. In addition, a full understanding of the potential aircraft impacts requires that the abundance, composition and formation mechanisms of the particles themselves be established. Over the last three years with support from the High Speed Research Program, we have performed laboratory experiments to determine the chemical composition, formation mechanism, and reactivity of stratospheric aerosols.

## RESULTS AND DISCUSSION

### I. Heterogeneous Reactivity of Stratospheric Sulfate Aerosols

We have studied the heterogeneous reactions of  $\text{ClONO}_2$ ,  $\text{N}_2\text{O}_5$  and  $\text{CH}_2\text{O}$  on sulfuric acid surfaces representative of the global sulfate aerosol layer [1, 2]. We found that the hydrolysis of  $\text{ClONO}_2$  on sulfuric acid was a strong function of the wt%  $\text{H}_2\text{SO}_4$ , with a much more rapid reaction for more dilute sulfuric acid [1]. This important chlorine activation reaction will thus be most important at low atmospheric temperatures where the sulfuric acid is more dilute. In contrast, we found that the hydrolysis of  $\text{N}_2\text{O}_5$  was rapid on sulfuric acid of all concentrations, even up to 95 wt%  $\text{H}_2\text{SO}_4$ . Thus inclusion of this reaction is critical in modeling the global atmospheric effects of stratospheric aircraft. Inclusion of the  $\text{N}_2\text{O}_5$  reaction in atmospheric models has revealed that the main chemical family responsible for most of the ozone destruction in the lower stratosphere is not  $\text{NO}_x$  as previously thought, but rather is  $\text{HO}_x$ . Because of the importance of  $\text{HO}_x$  in controlling ozone amounts, we also investigated the heterogeneous reaction of  $\text{CH}_2\text{O}$  on sulfuric acid [2].  $\text{CH}_2\text{O}$  is one of the most important reservoir species for  $\text{HO}_x$  in the upper troposphere/lower stratosphere. We found that  $\text{CH}_2\text{O}$  did indeed undergo heterogeneous loss on sulfuric acid surfaces. In contrast to the  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  reactions, the  $\text{CH}_2\text{O}$  reaction rate increased with increasing wt% sulfuric acid. The full ramifications of heterogeneous loss of  $\text{HO}_x$  reservoir species on stratospheric aerosols have yet to be determined.

## II. Formation Mechanisms of Type I Polar Stratospheric Clouds

Type I polar stratospheric clouds (PSCs) contain nitric acid and form several degrees above the ice frost point. If type I PSCs grow to large sizes, they can sediment and remove  $\text{HNO}_3$  from the lower stratosphere. Because they provide a removal route for  $\text{NO}_y$ , it is critical to understand their formation mechanism for assessments of stratospheric aircraft. Type I PSCs are thought to nucleate and grow on the background stratospheric sulfate aerosols (SSAs). To model this system, we exposed thin sulfuric acid films to water and nitric acid vapors while slowing cooling. FTIR spectroscopy was used to probe the phase of the sulfuric acid and to identify the  $\text{HNO}_3/\text{H}_2\text{O}$  films that condensed as a function of saturation ratio [3]. We found that liquid sulfuric acid films readily take up  $\text{HNO}_3$  upon cooling, forming supercooled ternary solutions of  $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ . This finding is in accord with recent models showing type Ib PSCs are composed of such supercooled ternary solutions. In addition, we found that crystalline sulfuric acid tetrahydrate (SAT) was not a good nucleating surface for  $\text{HNO}_3/\text{H}_2\text{O}$  PSCs. Specifically, we observed that very high saturation ratios were needed before the thermodynamically stable nitric acid trihydrate (NAT) would nucleate on SAT. This implies that if the stratospheric sulfate aerosols were to freeze at some time during the winter, they would be less able to nucleate PSCs than if they remained liquid. Because of the importance of sulfuric acid phase in nucleating PSCs, we also studied the freezing [4, 5] and melting [4] behavior of sulfuric acid under stratospheric conditions. We found that thin films of sulfuric acid on a silicon support routinely froze to SAT when cooled under stratospheric conditions [4]. In contrast, studies using actual aerosol samples showed persistent supercooling of sulfuric acid without freezing [5]. These studies taken together imply that sulfuric acid aerosols will not freeze in the stratosphere via homogeneous nucleation, but may freeze readily if they contain a solid inclusion. In addition, melting studies [4] showed that SAT will not melt in the stratosphere until the temperature rises to above  $\sim 215$  K. Thus once SAT does form, it will persist for quite some time, and type I PSC formation will be hindered.

## III. Optical Detection of Polar Stratospheric Clouds

Because there are many factors that appear to influence the formation of PSCs, it is highly desirable to make field measurements of the phase and composition of actual particles in the atmosphere. Optical measurements of PSCs require accurate knowledge of the real and imaginary refractive indices of the possible PSC materials. We have used optical interference techniques to measure the real refractive index at  $\lambda = 632$  nm for  $\text{HNO}_3/\text{H}_2\text{O}$  films representative of type I PSCs [6, 7]. Refractive indices were measured for both amorphous and crystalline  $\text{HNO}_3/\text{H}_2\text{O}$  films. For the amorphous films, the refractive indices increased with increasing nitric acid content. The values range from  $n = 1.31$  for pure ice to  $n = 1.47$  for nearly pure nitric acid. Indices for crystalline  $\text{HNO}_3/\text{H}_2\text{O}$  films were substantially higher than for the amorphous analogs. We have also made measurements of the real and imaginary refractive indices for  $\text{HNO}_3/\text{H}_2\text{O}$  films in the infrared [8]. In addition, we have used these infrared optical constants to analyze solar extinction data for type I PSCs observed in September, 1987 over Antarctica [9]. We found that these PSCs were not fit well by any of the measured infrared optical constants. This suggests that these PSCs

were not composed of NAT, as had been commonly assumed. These findings are consistent with type I PSCs composed of supercooled ternary solutions, although the optical constants for such solutions are not yet available.

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